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<b>(21) International Application Number:</b> PCT/US94/05826 <b>(22) International Filing Date:</b> 24 May 1994 (24.05.94)  <b>(30) Priority Data:</b> 068,975 28 May 1993 (28.05.93) US  <b>(71) Applicant:</b> POTTERS INDUSTRIES INC. [US/US]; Corporate Technical Center, 600 Industrial Road, P.O. Box 6626, Carlstadt, NJ 07072 (US).  <b>(72) Inventor:</b> SCHLEIFSTEIN, Robert, A.; 27 Deborah Drive, Edison, NJ 08820 (US).  <b>(74) Agents:</b> SNYDER, George, B. et al.; Curtis, Morris & Safford, 530 Fifth Avenue, New York, NY 10036 (US).		<b>(81) Designated States:</b> AU, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).  <b>Published</b> <i>With international search report.</i>
<b>(54) Title:</b> CATALYST COATED BEADS FOR CURING POLYESTER RESIN  <b>(57) Abstract</b>  As an article of manufacture, stable particles containing, in combination, inorganic filler material, benzoyl peroxide and a non-hygroscopic stabilizer for benzoyl peroxide; their production; and the formation of a polymeric matrix with such particulate matter.		

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## CATALYST COATED BEADS FOR CURING POLYESTER RESIN

FIELD OF THE INVENTION

This invention relates to catalyst-bearing particles, especially inorganic filler material coated with benzoyl peroxide, their production and the formation of a polymeric matrix with such particulate matter.

BACKGROUND OF THE INVENTION

Inorganic filler material, particularly vitreous beads, are widely used as additives in polymeric compositions, such as those deposited on highways to provide reflective markers, for instance, edge and lane striping, signs, etc. As is well known, it has become common practice to drop small glass spheres onto a painted line on a highway while the paint is still tacky such that the spheres are partially embedded in the paint when it has dried. The spheres render the line or other marker retroreflective and reflect the light from headlights so that the marker is more visible to the motorist. In some cases the spheres are embedded in spherical or irregularly shaped plastic granules prior to being contacted with the paint in the manner disclosed in U.S. Patent Nos. 3,252,376 and 3,254,563, for example, in an effort further to improve the reflectivity of the marker.

It is also known to provide inorganic filler material having a catalyst fixed to the surface of the filler material to effect polymerization of a polymerizable material upon contact of the catalyst-containing filler material with the polymerizable material in the manner disclosed in British published patent application 88 10 801.4. The catalyst is fixed to the surface of the filler material by means of a fixing agent adhered to the filler material. A particularly preferred catalyst is benzoyl peroxide. However, it appears that particulate material containing benzoyl peroxide and the fixing agents disclosed in such patent

application could have been rendered unstable by the use of organic liquids. These solvents and/or binding agents could have destabilized the benzoyl peroxide dispersion as they bound the benzoyl peroxide to the filler surface.

5 The incorporation of conventional stabilizing agents for benzoyl peroxide, such as taught in U.S. Patent No. 4,917,816, in order to give some stability to the particulate material yields particles which, in volume quantities, do not have good flowability.

10 It would be a substantial advance to provide inorganic filler material incorporating benzoyl peroxide catalyst, which is both stable and free-flowing for convenient processing, and effects catalysis of the curing of a polymerizable material in which the filler  
15 material is included.

#### OBJECTS OF THE INVENTION

It is thus an object of the invention to provide an article of manufacture comprising an inorganic filler material which effectively catalyzes the curing of  
20 polymerizable material in which it is included.

It is a further object of the invention to provide an article of manufacture comprising a stable particle of inorganic filler material incorporating benzoyl peroxide.

25 It is another object of the invention to provide, as an article of manufacture, a free-flowing particulate matter containing inorganic filler material and benzoyl peroxide.

A further object of the invention is to provide  
30 methods of forming such article of manufacture, and methods of forming a polymeric matrix using such article of manufacture.

These and other objects of the invention will be readily apparent from the following description and  
35 claims.

SUMMARY OF THE INVENTION

In one aspect, the present invention is an article of manufacture comprising a stable particle containing, in combination, inorganic filler material, benzoyl peroxide and a non-hygroscopic stabilizer for benzoyl peroxide. The composition can further contain an accelerator for benzoyl peroxide catalytic activity or a surfactant. Advantageously, the surfactant facilitates adherence, especially direct adherence, of the benzoyl peroxide to the inorganic filler material without itself effecting such adherence.

In another aspect, the present invention is a multiplicity of stable catalyst-bearing particles, each of said particles containing inorganic filler material, benzoyl peroxide and a non-hygroscopic stabilizer for benzoyl peroxide, said multiplicity of particles being free-flowing.

In several especially advantageous embodiments, the particle consists essentially of inorganic filler material, benzoyl peroxide adhered directly to said inorganic filler material, a metal-free and silane-free surfactant for facilitating adherence of the benzoyl peroxide to the inorganic filler material without itself effecting such adherence, and a non-hygroscopic stabilizer for benzoyl peroxide. In other good embodiments multiplicity of such particles is provided.

The invention is also a method of forming a stable catalyst-bearing filler particle by combining inorganic filler material, benzoyl peroxide and a non-hygroscopic stabilizer for benzoyl peroxide. Advantageously, the method includes the steps of combining a particle of inorganic filler material and a metal-free, silane-free surfactant, and contacting the surfactant-treated particle with benzoyl peroxide and a non-hygroscopic stabilizer for benzoyl peroxide.

In addition, the invention is a method of forming a polymeric matrix by addition-polymerization via

the steps of distributing in an addition-polymerizable material a multiplicity of stable catalyst-bearing filler particles, and subjecting the addition-polymerizable material containing the filler particles to conditions  
5 suitable for forming a polymeric matrix by addition-polymerization. In particular, the particles consist essentially of inorganic filler material, benzoyl peroxide adhered directly to said inorganic filler material, a metal-free and silane-free surfactant for  
10 facilitating adherence of the benzoyl peroxide to the inorganic filler material without itself effecting such adherence, and a non-hygroscopic stabilizer for benzoyl peroxide.

Practice of the invention enables realization  
15 of several important advantages. The use of catalyst coated beads for curing polyester resin allows simplified application of glass beads, polyester paint and catalyst for preparing road markings. In particular, the disadvantageous step of separately applying liquid  
20 peroxide catalyst for curing the polyester paint is avoided. Furthermore, the catalyst-bearing particles of the present invention incorporate an advantageously stabilized catalyst, avoiding the use of prior inorganic filler materials having peroxide catalyst fixed to the  
25 surface thereof. Moreover, the catalyst-bearing particles of the present invention are advantageously free-flowing, providing a significant benefit especially under humid application conditions.

#### DESCRIPTION OF CERTAIN PREFERRED EMBODIMENTS

30 A central aspect of the invention is the use of a non-hygroscopic stabilizer. This is generally a salt which does not release water of hydration when held for any appreciable time (such as the time necessary for drying of the catalyst) at 50°C or less. This enables  
35 the attainment of catalyst coated particulate material which has good flowability, and is in favorable contrast to the use of conventional stabilizers of the hygroscopic

variety. As it turns out, the use of hygroscopic materials causes the catalyst coated particles to clump or otherwise agglomerate in such manner as to be unacceptably resistant to flow.

5 Another important feature of the claimed invention is the uniform application of tightly and directly adherent catalyst to the bead. By "adherent" is meant that the catalyst is held firmly against the inorganic filler material; while not intending to be  
10 bound by the following theory, I believe that the "adherence" is principally physical in that the catalyst uniformly coats the inorganic filler material and that the intrinsic structural integrity of the coating (upon drying and hardening) maintains that coating in effective  
15 contacting relationship with the inorganic filler material. (Of course, it will be appreciated that there can be surfactant and/or stabilizer deposits interposed between the coating and the inorganic filler material, but this is embraced within the meaning of the concepts  
20 "direct" and "effective contacting relationship".) The thrust of this is that the catalyst stays on the inorganic filler material without the need for linking the two together via a binding agent. Rather, it has been discovered that the benzoyl peroxide catalyst can be  
25 conveniently, substantially uniformly and permanently applied to the inorganic filler material by first "wetting" the material with a surfactant (for instance, a dispersion of surfactant in water) to promote its receptivity to the catalyst, contacting the surfactant-treated material with benzoyl peroxide and a stabilizer,  
30 and "baking" (i.e., heating) the material at a temperature sufficient to dry the catalyst on to the inorganic filler material. By practice of the invention, catalyst is adhered directly and substantially uniformly  
35 to the surface of the inorganic filler material. Typically, the heating is conducted at a temperature of

from 35 to 50°C for a time sufficient to effect drying and hardening of the catalyst.

The advantage of proceeding in accordance with the invention is that the use of a binding agent is avoided. The use of a binding agent can be detrimental because such conventional ones as silanes are in effect thermosetting materials which tend to "shrink" when curing upon heating, which causes the catalyst linked thereto to coalesce into globules on the inorganic filler material. This is, of course, antithetical to securing the uniformity of catalyst coating desired, and further leads to flaking off of the catalyst globules.

Yet another important feature is the rapid cure of the polymerizable material (e.g., the polyester resin paint) provided by the present invention without use of specialized application equipment. The use of catalyst-containing filler material in accordance with the instant invention is beneficial because the tightly adherent catalyst remains on the particle, rather than flaking off, and is therefore, uniformly distributed throughout the polymerizable material for maximum speed and effectiveness. In this connection, each of the particles of filler material is advantageously uniformly coated with the catalyst for increased distribution of catalyst on a local basis.

The present invention is directed to the deposition of catalyst on inorganic glass filler materials which are non-hygroscopic. Glasses such as A-glass (soda lime glass), C-glass (chemically resistant glass) and E-glass (borosilicate glass) are included. Also, other non-hygroscopic materials such as ceramics are contemplated. The catalyst is incorporated in an amount of from 0.4 to 2 percent based on the weight of the inorganic filler material.

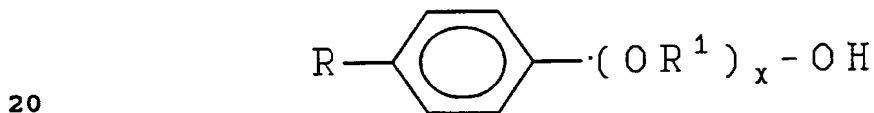
Preferably, the stabilizer is a salt containing water of hydration within a crystal lattice. In particular, the stabilizer is  $\text{CaSO}_4 \cdot n\text{H}_2\text{O}$ , wherein n is



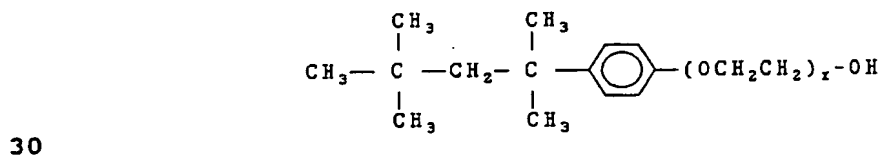
from 0.5 to 2, such as gypsum ( $n = 2$ ) or plaster of paris ( $n = 0.5$ ), aluminum oxide tri-hydrate or magnesium hydroxide. The stabilizer is typically included in the catalyst coated particle in an amount effective to  
 5 prevent unwanted rapid decomposition of the benzoyl peroxide, preferably, from 0.1 to 1.0 percent based on the weight of the inorganic filler material.

The accelerator, if one is used, can be any suitable conventional substance. Typically, the  
 10 accelerator for benzoyl peroxide catalytic activity is  $\text{NaH}_2\text{PO}_4 \cdot \text{H}_2\text{O}$  or  $\text{Na}_2\text{HPO}_4 \cdot 7\text{H}_2\text{O}$ .

The surfactant can be generally a non-ionic surfactant which is suitable for "wetting" the surface of the inorganic filler material to obtain the desired  
 15 amount of catalyst deposited thereon. In several good embodiments of the invention the surfactant is a compound of the formula



wherein R is hydrogen or  $\text{C}_n\text{H}_{2n+1}$ , or an aromatic moiety with a hydrophobic terminal group, such as  $\text{C}_8\text{-C}_{12}$  aliphatic;  $\text{R}^1$  is  $\text{C}_n\text{H}_{2n}$ , or can be a linear or branched  
 25 alcohol of  $\text{C}_9\text{-C}_{15}$ ; x is 4 to 40 (preferably 6-10); and n is 1 to 20, particularly a compound of the formula



wherein x is 6 to 10. The surfactant is incorporated in the catalyst-coated particle in an amount which is commensurate with the amount necessary to achieve the desired amount of catalyst deposition on the inorganic  
 35 filler material's surface, preferably .05-0.5 percent based on the weight of the inorganic filler material, especially about 0.2 percent. (It will be on the weight

of the IFM appreciated that the amount of surfactant and stabilizer incorporated in the catalyst coated particles will typically increase, all other things being equal, with a decrease in particle size as each particle will  
5 thus have more surface area.)

Unsaturated polyester resin syrups which may be catalyzed by the peroxide compositions of the present invention include unsaturated polyester resins having a copolymerizable monomer which contains a terminal vinyl  
10 group. The unsaturated polyester resin may be derived from the polyesterification of a polycarboxylic acid or a polycarboxylic acid anhydride with a polyol according to techniques well known to those skilled in the art. Since the polyester resin to be produced is unsaturated, the  
15 polycarboxylic acid or anhydride, the polyol, or both must contain at least one ethylenically unsaturated bond in the structure.

The polyester resins, for example, in general are formed by the reaction of one or more dicarboxylic  
20 acid components and one or more polyhydric alcohols. Illustrative dicarboxylic acid components include saturated anhydrides and adipic and azelaic acids, and the unsaturated components fumaric acid and maleic acid. The commonly used dihydric alcohols include glycols of  
25 ethylene, propylene, 1,3- and 2,3-butylene, diethylene and dipropylene. The polyester reaction products are mixed with an unsaturated monomeric cross-linking agent for the polyester resin such as styrene. Other materials that may be employed as a monomeric agent include methyl  
30 methacrylate, vinyl toluene, vinyl acetate, ortho and para methyl styrene, divinyl benzene, ethyl acrylate and many others. The monomeric agent is of the nature such that it is consumed during the curing of the resin without forming volatile materials.

35 Typically, the inorganic filler material and the surfactant are mixed together in a rotary mixer, to which the catalyst and stabilizer are then added;

however, other mixing apparatus which is capable of effectively administering these components (especially the heavy mixture of all of them combined) is suitable. The amount of surfactant, catalyst and stabilizer used is  
5 sufficient to yield an amount of each such component in the catalyst coated particle falling within the ranges disclosed in preceding paragraphs.

The present invention is further described and illustrated in the following examples. Further objects  
10 of this invention, together with additional features contributing thereto and advantages accruing therefrom, will be apparent from the following examples of the invention. It will be appreciated that variations and modifications to the products and methods can be made by  
15 the skilled person without departing from the spirit or scope of the invention as defined in the appended claims.

EXAMPLE 1

One hundred pounds of glass beads as inorganic filler material was charged into a clean stainless steel  
20 tumbler. The tumbler had an explosion-proof motor and heating system. Proper ventilation was provided. Tumbling of the beads was begun without heating.

Triton X-100 (commercially available from Union Carbide Corp.) surfactant, pre-diluted to a 20 weight  
25 percent solution, was added to the tumbler in an amount of 113.5 grams of surfactant per 100 pounds of beads (corresponding to 567.5 grams of water and 113.5 grams of Triton X-100 per 100 pounds of beads). The mixture was tumbled for several minutes.

30 Gypsum-stabilized benzoyl peroxide (commercially available under the name Abcat 40 from ABCO Industries, Inc., Roebuck, SC) was slowly added to the tumbler over several minutes in an amount of three pounds of Abcat 40 per 100 pounds of beads. The beads were now  
35 very wet and heavy.

The coated beads were heated as fast as possible to a temperature of 45-50°C. The beads were held at this temperature for five minutes.

The beads were homogeneously coated with a smooth and even benzoyl peroxide coating.

#### EXAMPLE 2

The beads of Example 1 were exposed overnight to an atmosphere of 95°F and 94% relative humidity. The beads did not produce a "wet-sand" texture and remained free-flowing.

#### EXAMPLE 3

Cure rates were compared using conventionally stabilized benzoyl peroxide (commercially available under the name Abcure 40-25 from ABCO Industries, Inc., Roebuck, SC) and using benzoyl peroxide stabilized with a non-hygroscopic stabilizer according to the present invention.

To 10 grams of resin, either 0.3 grams of the conventionally stabilized benzoyl peroxide (Abcure 40-25) were added or 0.3 grams of benzoyl peroxide stabilized with a non-hygroscopic stabilizer in accordance with the present invention were added.

Cure times were observed at 78°F. The results were as follows:

	<u>Catalyst</u>	<u>Initial Cure Time (Min.)</u>	<u>Final Cure Time (Min.)</u>
25	Abcat 40	2.33	3.46
30	Abcure S-40-25	6.13	7.70

This shows that the benzoyl peroxide catalyst stabilized by the non-hygroscopic stabilizer in accordance with the present invention provided superior cure time compared with a conventionally stabilized benzoyl peroxide catalyst.

**EXAMPLE 4**

Cure times for 10 grams of beads coated with 3% Abcat 40 dispersion, blended with 10 grams of styrenated unsaturated polyester resin were as follows:

5		<u>Final</u>
	<u>Sample No.</u>	<u>Cure Time</u>
		(Min.)
	Run #1	4.02
10	Run #2	3.85

These cures times approached those obtained with Abcat 40 shown in Example 3.

**COMPARATIVE EXAMPLE 5**

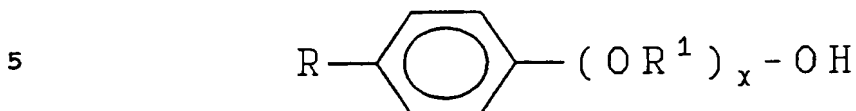
15 Abcure S-40-25 coated beads were too clumped together for testing within 12 hours after coating.

WHAT IS CLAIMED IS:

1. As an article of manufacture, a stable particle which comprises in combination inorganic filler material,  
5 benzoyl peroxide and  
a non-hygroscopic stabilizer for benzoyl peroxide.
2. As an article of manufacture, the stable particle as claimed in claim 1, wherein the stabilizer is  
10 a salt containing water of hydration within a crystal lattice.
3. As an article of manufacture, the stable particle as claimed in claim 2, wherein the stabilizer is gypsum.
- 15 4. As an article of manufacture, the stable particle as claimed in claim 2, wherein the stabilizer is  $\text{CaSO}_4 \cdot n\text{H}_2\text{O}$ , wherein n is from 0.5 to 2.
5. As an article of manufacture, the stable particle as claimed in claim 1, further comprising an  
20 accelerator for benzoyl peroxide catalytic activity.
6. As an article of manufacture, the stable particle as claimed in claim 5, wherein the accelerator is  $\text{NaH}_2\text{PO}_4 \cdot \text{H}_2\text{O}$  or  $\text{Na}_2\text{HPO}_4 \cdot 7\text{H}_2\text{O}$ .
7. As an article of manufacture, the stable  
25 particle as claimed in claim 1, wherein the inorganic filler material is a vitreous bead.
8. As an article of manufacture, the stable particle as claimed in claim 1, further comprising a  
surfactant.

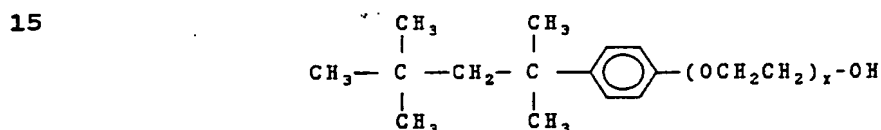
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9. As an article of manufacture, the stable particle as claimed in claim 8, wherein the surfactant is a compound of the formula



wherein R is hydrogen or  $\text{C}_n\text{H}_{2n+1}$ , or an aromatic moiety with a hydrophobic terminal group,  $\text{R}^1$  is  $\text{C}_n\text{H}_{2n}$  or a linear  
10 or branched alcohol of  $\text{C}_9$ - $\text{C}_{15}$ , x is 4 to 40 and n is 1 to 20.

10. As an article of manufacture, the stable particle as claimed in claim 9, wherein the surfactant is a compound of the formula



wherein x is 6 to 10.

20 11. A multiplicity of catalyst-bearing particles, each of said particles comprising inorganic filler material, benzoyl peroxide and a non-hygroscopic stabilizer for benzoyl peroxide,

25 said multiplicity of particles being free-flowing.

12. As an article of manufacture, a stable particle which consists essentially of, in combination, inorganic filler material;

30 benzoyl peroxide adhered directly to said inorganic filler material;

a metal-free and silane-free surfactant for facilitating adherence of the benzoyl peroxide to the inorganic filler material without itself effecting such adherence; and

35 a non-hygroscopic stabilizer for benzoyl peroxide.

13. A multiplicity of stable catalyst-bearing particles, each of which consists essentially of inorganic filler material; benzoyl peroxide adhered directly to said inorganic filler material; a metal-free and silane-free surfactant for facilitating adherence of the benzoyl peroxide to the inorganic filler material without itself effecting such adherence; and a non-hygroscopic stabilizer for benzoyl peroxide; said multiplicity of particles being free-flowing.
14. A composition which comprises benzoyl peroxide and a non-hygroscopic stabilizer for benzoyl peroxide on a substantially free-flowing inorganic filler.
15. A method of forming a stable catalyst-bearing filler particle, which comprises combining inorganic filler material, benzoyl peroxide and a non-hygroscopic stabilizer for benzoyl peroxide.
16. A method of forming a stable catalyst-bearing filler particle, which comprises combining a particle of inorganic filler material and a metal-free, silane-free surfactant, and contacting the surfactant-treated particle with benzoyl peroxide and a non-hygroscopic stabilizer for benzoyl peroxide.
17. A method of forming a polymeric matrix by addition-polymerization, which method comprises contacting an addition-polymerizable material with an article of manufacture comprising in combination a particle of inorganic filler material, benzoyl peroxide and a non-hygroscopic stabilizer for benzoyl peroxide.
18. A method as claimed in claim 17, wherein the stabilizer is a salt containing water of hydration within a crystal lattice.



15

19. A method as claimed in claim 18, wherein the stabilizer is gypsum.

20. A method as claimed in claim 18, wherein the stabilizer is  $\text{CaSO}_4 \cdot n\text{H}_2\text{O}$ , wherein n is from 0.5 to 2.

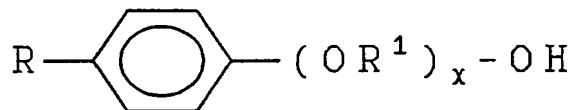
5 21. A method as claimed in claim 17, further comprising an accelerator for the addition-polymerization.

22. A method as claimed in claim 21, wherein the accelerator is  $\text{NaH}_2\text{PO}_4 \cdot \text{H}_2\text{O}$  or  $\text{Na}_2\text{HPO}_4 \cdot 7\text{H}_2\text{O}$ .

10 23. A method as claimed in claim 17, wherein the particle of inorganic filler is a vitreous bead.

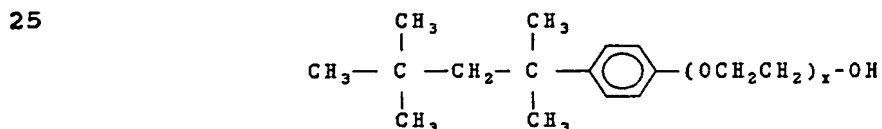
24. A method as claimed in claim 17, further comprising a surfactant.

15 25. A method as claimed in claim 24, wherein the surfactant is a compound of the formula



20 wherein R is hydrogen or  $\text{C}_n\text{H}_{2n+1}$  or an aromatic moiety with a hydrophobic terminal group,  $\text{R}^1$  is  $\text{C}_n\text{H}_{2n}$  or a linear or branched alcohol of  $\text{C}_9$ - $\text{C}_{15}$ , x is 4 to 40 and n is 1 to 20.

26. A method as claimed in claim 25, wherein the surfactant is a compound of the formula



wherein x is 6 to 10.

30

27. A method of forming a polymeric matrix by addition-polymerization, which consists essentially of distributing in an addition-polymerizable material a multiplicity of stable catalyst-bearing filler particles, each of said particles consisting essentially of inorganic filler material, benzoyl peroxide adhered directly to said inorganic filler material, a metal-free and silane-free surfactant for facilitating adherence of the benzoyl peroxide to the inorganic filler material without itself effecting such adherence, and a non-hygroscopic stabilizer for benzoyl peroxide, and subjecting said addition-polymerizable material containing said filler particles to conditions suitable for forming a polymeric matrix by addition-polymerization.

## INTERNATIONAL SEARCH REPORT

 International application No.  
PCT/US94/05826

## A. CLASSIFICATION OF SUBJECT MATTER

IPC(5) :C08F 4/34; C08K 7/16

US CL :Please See Extra Sheet.

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 526/86, 109, 123, 184, 210, 227, 232.1, 902, 903, 908; 523/223; 524/736, 799, 788

 Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched  
NONE

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

APS: POLYMERIZATION CATALYST; BENZOYL PEROXIDE, HYGROSCOPIC FILLER

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US, A, 3,252,376 (VRIES) 24 May 1966, see entire document.	1-27
A	US, A, 3,254,563 (VRIES) 07 June 1966, see entire document.	1-27

☐ Further documents are listed in the continuation of Box C.
 ☐ See patent family annex.

* Special categories of cited documents:		*T	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
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*E	earlier document published on or after the international filing date	*Y	document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
*L	document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	*G	document member of the same patent family
*O	document referring to an oral disclosure, use, exhibition or other means		
*P	document published prior to the international filing date but later than the priority date claimed		

Date of the actual completion of the international search 14 JULY 1994	Date of mailing of the international search report 16 AUG 1994
Name and mailing address of the ISA/US Commissioner of Patents and Trademarks Box PCT Washington, D.C. 20231 Facsimile No. (703) 305-3230	Authorized officer SAMUEL A. ACQUAH Telephone No. (703) 308-2351

# INTERNATIONAL SEARCH REPORT

International application No.

PCT/US94/05826

## A. CLASSIFICATION OF SUBJECT MATTER:

US CL :

526/86, 109, 123, 184, 210, 227, 232.1, 902, 903; 523/223; 524/736, 799, 788